

THE EFFECTS OF MOLECULAR SATURATION
OF FEEDSTOCKS ON RENEWABLE DIESEL
PRODUCTION IN THE ABSENCE OF HYDROGEN GAS

By

Jonathan Dubinsky
B.S., University of Kansas, Environmental Science

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Masters of Engineering
Civil Engineering

2013

This Thesis for the Master of Engineering degree by

Jonathan Dubinsky

has been approved for the

Civil Engineering Program

by

Arunprakash Karunanithi, Chair

Ron Roher

Jason Ren

April 16, 2013

Dubinsky, Jonathan (MEng, Civil Engineering)

The Effects of Molecular Saturation of Feedstocks on Renewable Diesel Production in the Absence of Hydrogen Gas

Thesis directed by Assistant Professor Arunprakash Karunanithi

ABSTRACT

Catalytic deoxygenation of fatty acids was carried out using Palladium on Carbon (Pd/C) and Magnesium Oxide (MG70) catalysts and a Parr bench top micro reactor. The effect of feedstock saturation on the decarboxylation reaction was measured by varying the feedstock from stearic acid (fully saturated) to oleic acid (mono-unsaturated) to linoleic acid (poly-unsaturated). The prevalence of the decarboxylation reaction was measured by analyzing both the liquid products and the gaseous products. The liquid products were collected and analyzed for the major product, heptadecane (C₁₇), as well as straight chain alkane in the diesel range content using a gas chromatograph with a flame ionization detector. Concentration of CO₂ in the gaseous product was analyzed using gas chromatography. As saturation increased, the concentration of CO₂ in the gas phase increased, showing that decarboxylation occurred. The analysis of the liquid products showed as feedstock saturation increased the concentration of saturated straight chain hydrocarbons in the diesel fuel range with high selectivity to C₁₇ heptadecane increased, confirming that the decarboxylation reaction favors more saturated feedstocks.

The form of and content of this abstract are approved. I recommend its publication.
Approved: Arunprakash Karunanithi

DEDICATION

I dedicate this work to my loving and supportive sweetheart, Elizabeth. She has encouraged me to always pursue my dreams with confidence and grace.

ACKNOWLEDMENTS

It is with great honor that I am able to contribute this paper to the scientific community. As an owner and operator of a vegetable oil powered educational bus, I have seen first hand the power and limitations of alternative fuel sources. I would like to thank Dr. Arun Karunanithi for going out on a limb and taking on a greasy mechanic like myself. I would like to thank my parents for being the change that they want to see in the world, and always telling me that I can do what ever I put my mind to. Thank you to all the merry pranksters and joy seekers in the world...you know who you are. I plan to not only work to advance the field of bio-fuels technology, but to educate the next generation with the concepts of sustainability and biophilia. Long live spaceship Earth.

TABLE OF CONTENTS

CHAPTER

I	EXPERIMENTAL.....	1
	Introduction.....	1
	Background and Problem.....	1
	Biomass Based Diesel/Renewable Diesel.....	3
	Purpose of the Project	5
	Experimental	7
	Methods.....	7
	Chemicals and Catalysts	7
	Decarboxylation Reaction.....	8
	Analysis of Products	9
	Results.....	10
	Effects of Feedstock Saturation on Liquid Products.....	10
	Effects of Feedstock Saturation on Gaseous Products.....	15
	Discussion	16
II	ENVIRONMENTAL ASSESMENT	18
	Introduction.....	18
	Goal and Scope	19
	System Boundaries.....	19
	Process flow diagram.....	20
	Experimental Lab data	21
	Feedstock	22

Life Cycle Inventory	22
Allocations	22
Method of Data Collection.....	22
Decarboxylation Reaction Methods.....	23
Conversion Methods	24
Environmental Impact Assessment.....	24
Interpretation.....	28
Goal and Scope	28
Results and Discussion	29
III CONCLUSIONS.....	31
Significant Findings	31
Next Steps	32
REFERENCES	34
APPENDIX.....	38
Soybean Agriculture Unit Process Data	38
Soybean Transport Unit Process Data	39
Soybean Crushing Unit Process Data	40
Soybean Oil Transport Unit Process Data	41
Soybean Oil Conversion to Renewable Diesel using Hydrogen Process	42
Soybean Oil Conversion to Renewable Diesel using Non-Hydrogen Process	44

LIST OF TABLES

Table

1 This table show levels of saturation in some common feedstock oils	7
2 Concentration in mg/l of straight chain alkanes from C ₇ to C ₁₇ in the liquid products.	12
3 A collection of calculations needed to compute environmental impacts of biofuels. ..	24
4 Cradle-to-grave comparison of petroleum diesel, HDO renewable diesel and non- hydrogen renewable diesel.....	27
5 Soybean agriculture raw materials data	38
6 Soybean agriculture emissions data	38
7 Soybean transport raw materials data	39
8 Soybean transport emissions data	39
9 Soybean crushing raw materials data.....	40
10 Soybean crushing emissions data.....	41
11 Soybean transport data raw materials	41
12 Soybean transport emissions data	42
13 HDO raw materials data assuming an 84% yield	43
14 HDO emissions data assuming an 84% yield	43
15 Non-hydrogen raw materials data assuming a 45% yield.....	44
16 Non-hydrogen emissions data assuming a 45% yield.....	44

LIST OF FIGURES

Figure

1 Chemical formulas for three common biofuels: Biodiesel, Ethanol, and Renewable Diesel	3
2 This diagram, which was extracted from Bambang et al, 2011, shows the stoichiometry of the renewable diesel reaction.....	4
3 Summary of total expenses in a current HDO renewable diesel processing plant.	5
4 Stoichiometric equation for the decarboxylation reaction	6
5 This diagram, extracted and modified by from Kubickova, 2007, is of the Parr 4590 bench top reactor setup used in the experiment	9
6 These figures show the yield of both total fuel range alkanes and the major product heptadecane.....	12
7 GC chromatograms of alkane reaction products at 673 K.....	13
8 Concentration of liquid Alkanes in the liquid product.....	14
9 This chart shows the selectivity to C ₁₇ heptadecane in the total alkane product	14
10 Real time data of produced gas from the reaction.	15
11 This chart show the concentration of CO ₂ in the gaseous products from GC	16
12 Process Flow Diagram	20
13 Global Warming Potential Indicator	25
14 Carcinogenic Effects Indicator	26
15 Aquatic Eco Toxicity Indicator.....	26
16 This chart show the life cycle GHG emissions from cradle to grave of three pathways to fuel production normalized to petroleum diesel.	27

17 CO ₂ e emissions from only the processing stage of three possible pathways to diesel fuel.	28
---	----

CHAPTER I

EXPERIMENTAL

Introduction

Background and Problem

“If you are in a shipwreck and all the boats are gone, a piano top . . . that comes along makes a fortuitous life preserver. But this is not to say that the best way to design a life preserver is in the form of a piano top. I think that we are clinging to a great many piano tops in accepting yesterday’s fortuitous contrivings.”

— Buckminster Fuller [Critical Path, 1981]

Society is at a transition point and now we have an opportunity to re-design our energy future. With the uncertainty of the world’s oil supply, economic crisis, and global climate change all on the horizon, a suitable fuel replacement must be identified. Wind, solar, fuel cells, geo-thermal and other renewable energy sources will play a part in a diverse energy portfolio, but liquid fuels which work with current infrastructure must be utilized during the transition. Bio-fuels are a potential fit for a liquid fuel replacement, but rigorous study needs to be done to determine the true costs. An exponential increase in the consumption of such biofuels throughout the world has taken place in the past few years [Serrano-Ruiz et al, 2012].

Bio-fuels have existed for thousands of years. The first fuel source for humans was wood, which we utilized for heat and to cook our food. Wood, or cellulose, contains carbon, which is sequestered from the air using photosynthesis. As technology and human ingenuity grew, we figured out how to extract fats and oils from plants and

animals. This became our primary light source, which was a great advancement for humanity because it meant we did not have to use fire in the summer time just for a little light. Health wise, candles were a great improvement over the soot and smoke from a fire [Barnes et al, 2005]. Human kind, however, did not abandon the use of fire once they discovered candles. There was a need and a use for both. It was not until thousands of years later, with the discovery of fossil fuels, that civilization resorted to a one-size fits all fuel source.

Rudolf Diesel observed and disapproved of this back in the 1890's. His engine did not use petroleum but locally grown peanut oil. "The use of vegetable oils for engine fuels may seem insignificant today," Diesel said in 1912, "but such oils may become in the course of time as important as the petroleum and coal tar products of the present time" [Paula et al, 2011]. In the late 1800s, other engines were released on the market that ran on gasoline alone. However, the diesel engine could operate on many different fuels sources including coal dust, animal fats, vegetable oil, and petroleum. The problem that we face today is a growing demand for fossil fuels with a shrinking supply. Our economy is dependent on growth, which results in increased energy consumption. Since the early 20th century we have been designing our systems to be reliant on one source of fuel, oil, unlike Rudoulf Diesel's engine. The transportation sector of our society heavily relies on petroleum, which accounts for essentially all (96%) of the transportation energy [Serrano-Ruiz et al, 2012]. The natural world evolved to have biodiversity and resilience, the measure of which is an ecosystems ability to bounce back after a catastrophic event like a hurricane or a volcano. This ability to bounce back is now our great struggle as a human nation. We are now faced with the challenge of coming up with replacements to a

cheap hydrocarbon based system or face the slow sinking of our great ship and the frantic clinging to piano tops as we struggle to survive.

Biomass Based Diesel/Renewable Diesel

The commercial market for biodiesel is approximately 2.5 billion gallons per year and will grow rapidly in the near future due to the Renewable Fuels Standards (RFS-2), which establishes renewable fuel consumption and production mandates in the United States [EPA, 2012]. The global market for biofuels is expected to reach \$280 billion by the year 2022 [Solecki et al, 2011; REN21, 2011]. Renewable diesel, or Biomass Based Diesel, refers to fuel produced from biomass that has at least a 50% reduction in life cycle CO₂ emissions as compared to petroleum and can be used as a direct substitute (not blended) in internal combustion engines such as diesel, gasoline, or jet [EPA, 2012]. The chemical makeup of renewable diesel is exactly identical to petroleum, unlike other biofuels such as biodiesel and ethanol (see figure 1).

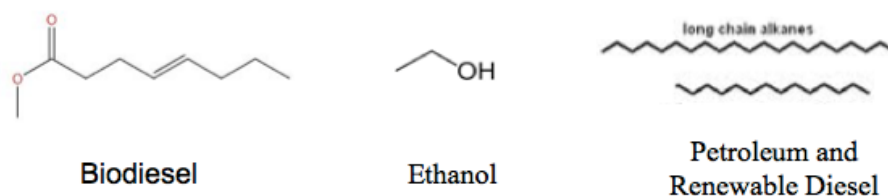


Figure 1 Chemical formulas for three common biofuels: Biodiesel, Ethanol, and Renewable Diesel

The most commonly known biofuel today is biodiesel or F.A.M.E (fatty acid methyl esters). This fuel has a chemical makeup that is compatible with diesel engines, but not identical to petroleum diesel [Mikulec et al, 2010]. In recent years a new biofuel based on pure hydrocarbons has been heavily researched. This differs from biodiesel significantly in molecular structure and production process. From an environmental

standpoint, both renewable diesel and biodiesel outperform petroleum diesel in all categories of emissions, including particulates, unburned hydrocarbons, NO_x, SO_x, and carbon monoxide [Kalnes et al, 2009]. This new class of “second generation” biofuels is referred to as Biomass Based Diesel or Renewable Diesel in the EPA’s Renewable Fuel Standards (RFS2) [EPA, 2012]. These fuels can come from diverse feedstocks such as vegetable oil, fats, algae oil, and waste oil. As opposed to biodiesel, which can only be used in a diesel engine, renewable diesel can be refined to make jet fuel, gasoline, green naphthalene, and other hydrocarbon based products [Knothe et al, 2010]. There are three major chemical pathways to remove oxygen from the fatty acids found in plant based lipids, and hence produce renewable hydrocarbons. Those pathways are hydrodeoxygenation, decarboxylation, and decarbonylation (see figure 2).

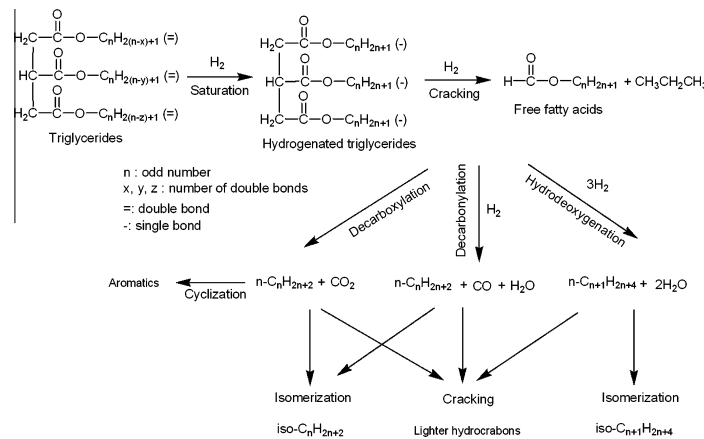


Figure 2 This diagram, which was extracted from Bambang et al, 2011, shows the stoichiometry of the renewable diesel reaction

The typical cascade reaction for upgrading triglycerides to hydrocarbon liquid fuels with three main routes: Decarboxylation, Decarbonylation, and Hydrodeoxygenation.

The major body of research on renewable diesel, and all current commercial endeavors, has been focused on the hydrodeoxygenation pathway, since it is most similar

to current refinery technology and has provided the highest yields of hydrocarbons [Šimáček et al, 2009; Huber et al, 2007; Veriansyah et al, 2012]. Other studies have looked just at the decarboxylation route or the decarbonylation route [Na et al, 2012; Rozmyszowicz et al, 2011]. One appeal to the decarboxylation route is that it does not consume hydrogen gas in the reaction, which is expensive and mainly produced from non-renewable sources [Abbasi et al, 2011]. Figure 3 clearly shows the high cost of hydrogen gas in the breakdown of capex and opex for a current commercial renewable diesel plant [Pearlson, 2011].

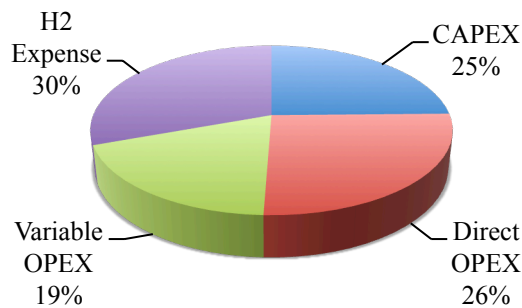


Figure 3 Summary of total expenses in a current HDO renewable diesel processing plant.

For each tonne of hydrogen produced from natural gas, approximately 2.5 tonnes of carbon is released as CO₂. When hydrogen is produced from coal, approximately 5 tonnes of carbon is emitted to the atmosphere per tonne of hydrogen. Currently over 90% of our hydrogen production comes from fossil fuels (coal, natural gas, and petroleum) [Abbasi et al, 2011].

Purpose of the Project

The goal of the project is to determine a safe, economic, and environmentally friendly means to convert biomass into renewable diesel that does not require large

amounts of hydrogen gas and hence is less expensive and safer. The project aims to assess the benefits of catalytic deoxygenation to convert lipids from non-food oil crops (e.g. camelina, castor bean, jatropha, and algae and waste biomass) into renewable diesel fuel through an energy densification process using thermal decarboxylation, which does not utilize molecular hydrogen, to deoxygenate lipids to hydrocarbon fuels. The reaction scheme for decarboxylation is presented in figure 4.

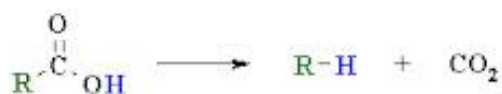


Figure 4 Stoichiometric equation for the decarboxylation reaction

This research looked at the impacts of lipid saturation on the extent of the decarboxylation reaction. Since feedstocks vary dramatically in fatty acid makeup, it was important for me to understand how saturation will impact the selectivity of the reaction towards our desired product. With this understanding it will allow operators to select appropriate feedstocks in their area as well as look into possible pre-treatment steps that end in desired saturation levels (see table 1). Algae oil also has the potential to be bred for desired traits such as saturation level [Schlagermann et al, 2010].

Table 1 This table show levels of saturation in some common feedstock oils

	Saturated	Monounsaturated	Polyunsaturated
	g/100g	g/100g	g/100g
Animal fats			
Lard	40.8	43.8	9.6
Duck fat	33.2	49.3	12.9
Butter	54	19.8	2.6
Vegetable fats			
Coconut oil	85.2	6.6	1.7
Palm oil	45.3	41.6	8.3
Cottonseed oil	25.5	21.3	48.1
Wheat germ oil	18.8	15.9	60.7
Soya oil	14.5	23.2	56.5
Olive oil	14	69.7	11.2
Corn oil	12.7	24.7	57.8
Sunflower oil	11.9	20.2	63
Safflower oil	10.2	12.6	72.1
Hemp oil	10	15	75
Canola/Rapeseed oil	5.3	64.3	24.8

Algae Species	Lipid Content	Saturated	Mono-Unsaturated	Poly-Unsaturated
	(% Dry Wt)	%	%	%
<i>Nannochloropsis salina</i>	31-68	45	35.2	20
<i>Botryococcus braunii</i>	25-75	26	5	62

In addition to the laboratory research, I also compared the environmental impacts of this process to hydrodeoxygenation and petroleum diesel using life cycle analysis and literature review. The main difference between the two pathways to renewable diesel is the use or non-use of hydrogen gas in the bio-fuel production process. The focus of the comparison was on energy requirements and GHG emissions of each process as well as other inputs and outputs deemed important by the industry and EPA.

Experimental

Methods

Chemicals and Catalysts

Oleic acid, stearic acid, and linoleic acid was purchased from Sigma Aldrich and used without further purification. A hydrocalcite solid phase powdered catalyst with

magnesium to alumina ratio of 70:30 (MG70) was purchased from Sasol. Palladium on activated carbon (Pd/C) with a 10% loading rate was purchased from Acros chemicals.

Decarboxylation Reaction

Several studies have previously explored the decarboxylation approach to renewable diesel production. The methods for this experiment were collected through rigorous literature review [Na et al, 2010; Na et al 2012; Rozmyszowicz et al, 2011; Snåre et al, 2007; Huber et al, 2007]. The decarboxylation reaction was performed using a Parr bench top stirred reactor (4590 micro reactor with a 100 ml reaction vessel and a 4848 controller). This batch reactor was customized for this reaction and fit underneath a chemical fume hood to evacuate any harmful gasses during sample ejection. The reactor was designed for a maximum pressure of 345 bar and 500 C with a flat graphite gasket. A multi blade impeller was purchased for mixing a liquid reactant with a solid phase catalyst. The temperature and pressure were plotted using the Parr software provided with the reactor. In one batch reaction 28g of reactant was placed in the reactor with 1.4g of catalyst (reactant catalyst=20:1). After loading the reactant and catalyst, the reactor was purged with nitrogen to remove any oxygen from the vessel. The purge method was based on standard procedures from literature [Kinsley et al, 2001]. After purging, the reactor was heated to 400 C and maintained until the reaction was completed. The reaction was monitored in real time using the pressure curve from the Parr software and was determined to be complete when the curve reached the upper asymptote (about 3 hours at 400 C and 4 hours total). Stirring speed was maintained at 150 rotations per minute during the reaction.

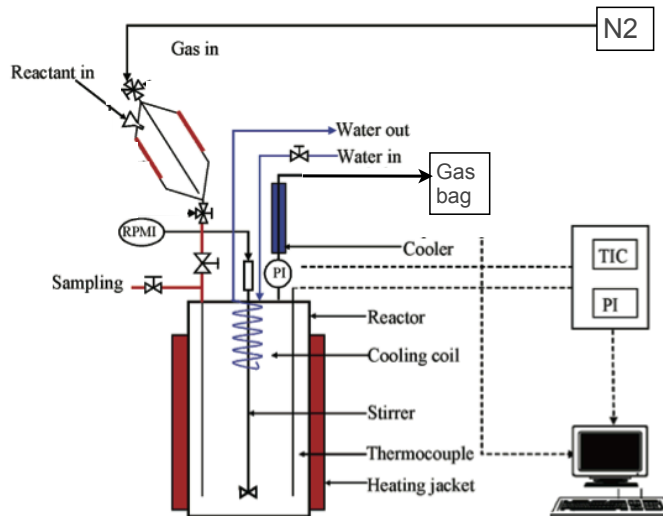


Figure 5 This diagram, extracted and modified by from Kubickova, 2007, is of the Parr 4590 bench top reactor setup used in the experiment

After completion the reactor was cooled down to 70 C using a customized cold water jacket (below this temperature unreacted stearic acid is solid). Then the gaseous products were collected in a tedlar bag and the liquid products were collected in a glass vial. A 1 ml sample of the liquid product was taken and dissolved in 25 ml of solvent (50/50 Dichloromethane and Acetone) and centrifuged at 5000 rpm for 5 minutes to separate any remaining catalyst. A polar and non-polar solvent was chosen because the unreacted starting material, fatty acids, are polar and the product, hydrocarbons, are non-polar.

Analysis of Products

The liquid products were first characterized using a Gas Chromatograph- Mass Spec (Shimadzu GC/MS-QP2010) equipped with a Restek 30m x 0.25mm x 0.5µm Rtx-Wax column. The carrier gas was helium and the flow rate was 1.0 ml/min. The column temperature was programmed to increase from 40 C to 240 C at 5 C/min. Samples were derivitized to protect the column from unreacted carboxylic acids using

Dimethylformamide dimethyl acetal and then dissolved in Dichloromethane before injection. After characterization of the products pure hydrocarbons standards, alkanes from C₆ to C₃₀, were obtained and calibration curves were developed for each individual alkane using a GC-FID. Peak areas and retention times were associated with known concentrations of pure samples. The liquid products from the reaction were then analyzed using a Thermo trace GC-FID equipped with a Restek 30m x 0.18mm x 0.18µm Rxi-1ms column for quantification of desired products. The carrier gas was helium and the flow rate was 2.75 ml/min. The column temperature was programmed to increase from 40 C to 330 C at a 20 C/min rate. The final temperature was held for 20 minutes and the FID base temperature was held at 350 C. The gas products were analyzed using a gas chromatograph (SRI 8610 C) equipped with an FID detector.

Results

Effects of Feedstock Saturation on Liquid Products

The chromatograms (GC results) of the liquid product analyses are presented in figure 7. The major product was heptadecane, C₁₇, and other minor products were alkanes from C₆ to C₁₇. Other hydrocarbons may be present in the product but were not considered in this study. Alkanes are viewed as more desirable over aromatics due to toxicity and suitability to diesel fuel [Senate, 2013; Kubic̃kova et al, 2005]. Straight chain alkanes also have a higher cetane number than aromatics, however isomers and cracked hydrocarbons have physical properties desirable for fuels such as lower cloud points [Huber et al, 2007]. For the purpose of this research, I only looked at straight chain alkanes. Since the feedstocks used have a carbon count of C₁₈ the main product was C₁₇, heptadecane, due to the decarboxylation reaction removing one carbon along with the O₂

molecule (see fig 4). Equation 1 shows how yield was calculated in the analysis. The reactants were fatty acids and the products were either heptadecane or total alkanes in the fuel range. Both results are presented in figure 6. Equation 2 shows how selectivity was calculated. Selectivity shows what percentage of the product was alkanes in the fuel range and then what percentage of the alkanes was the major product heptadecane. To do this, the mass concentrations from the GC were converted to volume % based on the mass and density of the different hydrocarbons. Both yield and selectivity were looked at in this study and the results are presented in figures 6, 8, 9.

$$\text{Yield} = \text{moles of recovered products} / \text{moles of reactants} \quad (1)$$

$$\text{Selectivity} = \text{volume of desired products} / \text{volume of total products} \quad (2)$$

The yield and selectivity for C₁₇ heptadecane was much higher when the Pd/C catalyst was used when compared to MG70. The results of the MG70 catalyst showed an even distribution among the fuel range hydrocarbons with a slightly higher concentration in the lighter range hydrocarbons. When Pd/C was used as the catalyst there was a clear increase in diesel range alkanes as feedstock saturation increased. Selectivity towards C₁₇ also increased when stearic acid was used as a feedstock when compared to oleic and linoleic acids. In addition to an overall increase in alkane yield and higher selectivity towards heptadecane, stearic acid had no peak for unreacted parent material in the chromatogram (fig 7). Overall Pd/C produced a higher concentration of diesel range hydrocarbons when compared to MG70. The concentrations of alkanes in the total liquid products (selectivity) from various experiments are presented in table 2 and figure 8.

Figure 8 represents various jars of product and shows what percentage of the jar is diesel range alkanes. It can be seen that as feedstock saturation increases, the percentage of the liquid product that is alkanes increased. Figure 9 is a similar chart, but looks at the selectivity of heptadecane amongst the alkanes. Again it can be seen as feedstock saturation increases, the percentage of the alkanes that is heptadecane increases. The selectivity for heptadecane when MG70 was used as a catalyst was non-existent. The product yield is also significantly lower then the product catalyzed by Pd/C.

Table 2 Concentration in mg/l of straight chain alkanes from C₇ to C₁₇ in the liquid products.

	Stearic (Pd/C)	Oleic (Pd/C)	Linoleic (Pd/C)	100% Oleic (MG70)
	mg/l	mg/l	mg/l	mg/l
Heptane	14029.048	15088.5805	8049.1225	14824.525
Octane	15839.248	15645.5755	8222.62675	16526.4135
Nonane	15218.82175	14777.687	6046.99825	11269.644
Decane	15031.03425	14747.7495	7193.92525	6221.37675
Undecane	13734.25925	13071.76	4612.82525	5830.232
Dodecane	13050.8775	10249.18875	3692.4235	5382.75375
Tridecane	12606.30125	9525.33875	3549.927	4092.063
Tetradecane	11817.1735	8099.932	2410.85525	3892.421
Pentadecane	14395.158	6995.4755	4898.19325	5864.8425
Hexadecane	5651.258	5241.062	3156.19	7240.094
Heptadecane	369051.304	211211.624	19603.772	5153.536
Total	500424.4835	324653.9735	71436.859	86297.9015
Total in (g/l)	500.4244835	324.6539735	71.436859	86.2979015

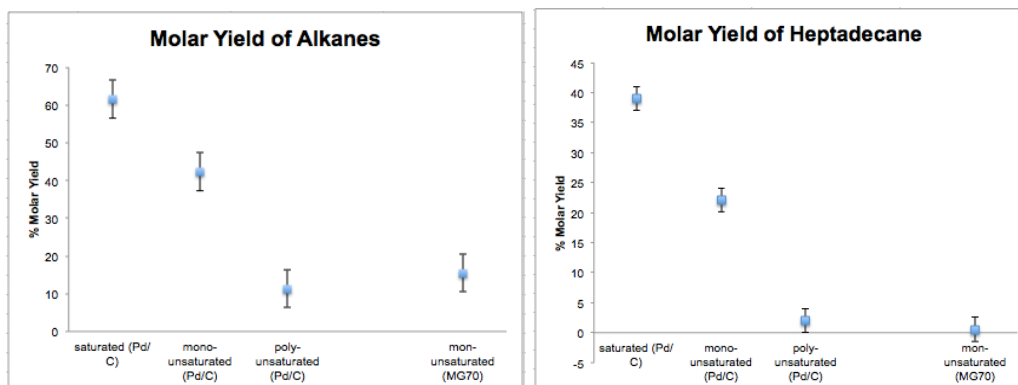


Figure 6 These figures show the yield of both total fuel range alkanes and the major product heptadecane.



Figure 7 GC chromatograms of alkane reaction products at 673 K

(1:hexane; 2:heptane; 3:octane; 4:nonane; 5: decane; 6: dodecane, 7: undecane; 8: tridecane; 9: tetradecane; 10: pentadecane; 11: hexadecane; 12: heptadecane; 13: oleic and stearic acid).

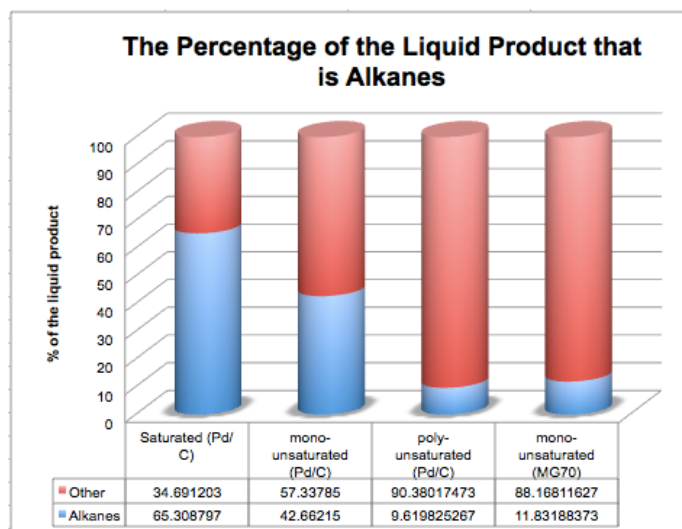


Figure 8 Concentration of liquid Alkanes in the liquid product

Each of the bars represent one liter of liquid product. The blue section of the bar is identified and quantified diesel range alkanes present in the product converted from mass per volume to volume per volume using the density of each component. The red sections are other compounds most likely made up of alkenes, aromatics, isomers, and unreacted feedstock.

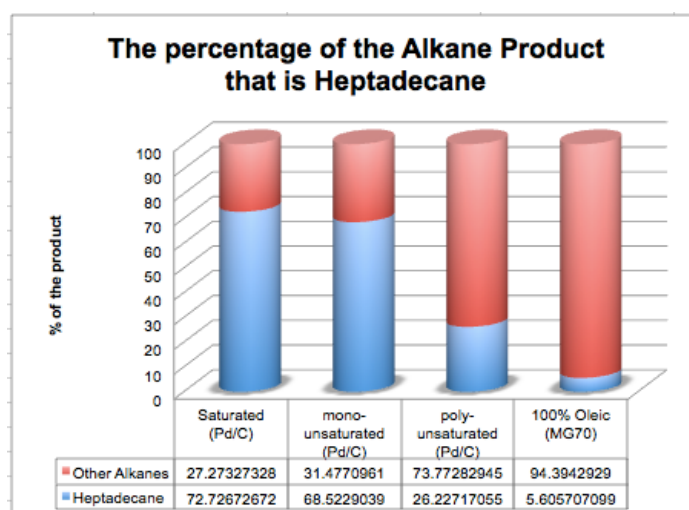


Figure 9 This chart shows the selectivity to C₁₇ heptadecane in the total alkane product

Each of the bars represent one liter of alkane product. The blue section of the bar is percentage of heptadecane present in the alkane product converted from mass per volume to volume per volume using the density of heptadecane. The red sections are other compounds made up of diesel range alkanes.

Effects of Feedstock Saturation on Gaseous Products

The gaseous products were collected, characterized, and quantified using GC and the results are presented in figures 10 and 11. After the gas was collected, it was left for 12 hours to cool and acclimate to room temperature and pressure. The total quantity was measured using the ideal gas law:

$$P_1 \cdot V_1 / T_1 = P_2 \cdot V_2 / T_2$$

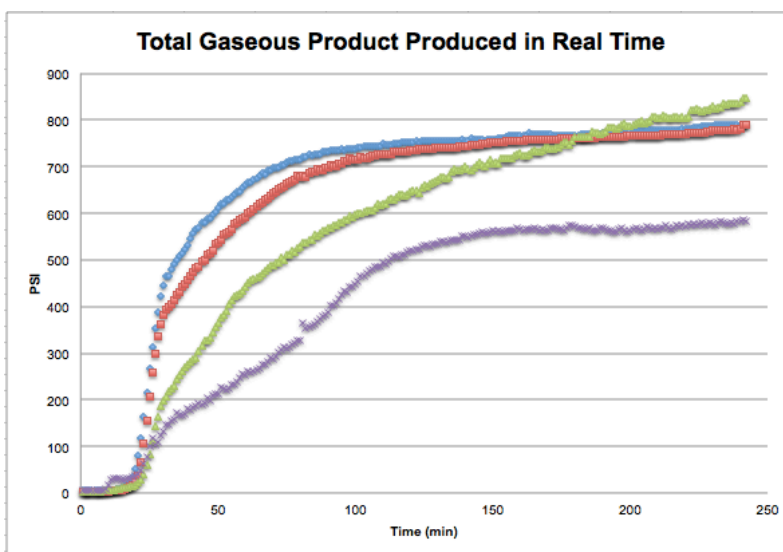


Figure 10 Real time data of produced gas from the reaction.

This graph shows pressure data from the reactor with varying levels of feedstock saturation and using two different catalysts (MG 70 and Pd/C). The reactor was cleared of all gasses before the reaction so this pressure curve relates to quantity of total gasses produced from the reaction. [blue=stearic (Pd/C), red = oleic (Pd/C), green=linoleic (Pd/C), purple=oleic (MG70)]

As you can see from figure 10, the pressure in the reactor increased more quickly with increasing feedstock saturation when the Pd/C catalyst was used. When the MG70 catalyst was used the overall quantity was much lower. The concentration of CO₂ in the

products was quantified by first injecting a known sample of CO₂ into the GC to develop a calibration curve. Then based on peak area, I was able to determine the concentration of CO₂ in the gaseous products. This value decreased as unsaturation in the feedstock increased, showing that the decarboxylation reaction, which produces CO₂, was more prevalent when a saturated feedstock was used. When MG70 was used as a catalyst, the CO₂ levels were much lower showing less decarboxylation occurred. This confirms that unsaturation of the feedstock leads to deactivation of the catalyst as well as a suppression of the decarboxylation reaction [Rozmyszowicz et al, 2011 pg 2818].

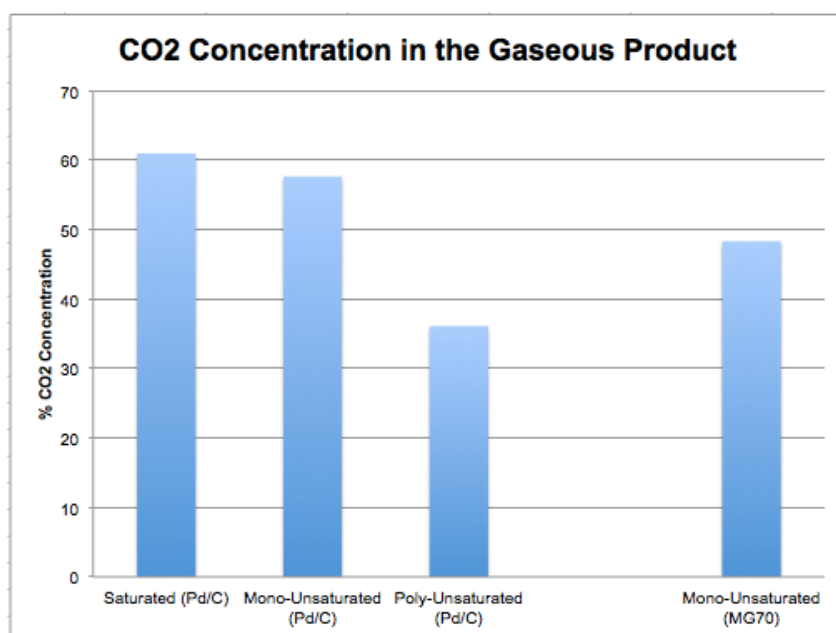


Figure 11 This chart show the concentration of CO₂ in the gaseous products from GC analysis

Discussion

From the results, we see that the decarboxylation reaction was more active based on both the liquid phase and gas phase analyses when the feedstock was more saturated. This is because the reaction order goes from hydrogenation to isomerization to

decarboxylation. When double bonds are present in the feedstock, they are susceptible to isomerization, hydrogenation, and aromatization reactions [Rozmyszowicz, 2011]. These reactions inhibit decarboxylation and therefore reduce the quantity of CO₂ and suppress the formation of desired alkanes. When oleic acid was used (one double bond) the tendency is for the molecule to become hydrogenated from H₂ produced in situ from side reactions to stearic acid and then to saturated alkanes. This is even more apparent with the use of linoleic acid (two double bonds). When a fully saturated feedstock such as stearic acid is used, the decarboxylation reaction happens much more quickly with fewer side reactions. This is also why stearic acid has higher selectivity to C₁₇ heptadecane when Pd/C is used as a catalyst. When the feedstock is saturated, the decarboxylation reaction happens much more quickly so cracking and isomerization are less prevalent, leading to a more predictable product based on the stoichiometric reaction. The fact that there is no remaining unreacted parent material in the product when stearic acid was used with Pd/C catalyst, also shows a more complete reaction scenario. There are still many undefined liquids in the samples that are most likely some combination of alkenes and aromatics as well as isomers of the parent material. Overall when MG70 was used, the reaction was much less complete and there was almost no selectivity to C₁₇ heptadecane. It was therefore concluded that PD/C is a much more effective catalyst for this reaction and no further study was done using MG70.

CHAPTER II

ENVIRONMENTAL ASSESMENT

Introduction

This chapter takes a brief look at the environmental impacts associated with renewable diesel production. This was not intended to be a full life cycle analysis on the production of renewable diesel. I coupled data found in the literature on life cycle analysis with data on yields from experimental research to compare two pathways for renewable diesel. This study was designed to see the value proposition and environmental potential in a hydrogen-free renewable diesel scenario. The main difference between the two pathways is the use or non-use of hydrogen gas in the bio-fuel production process. I focused on the non-hydrogen method because the hydrogen process has been well documented [Pearlson et al, 2011]. I have shown through laboratory experiments and environmental assessment that a viable alternative drop in replacement fuel can be produced without the use of hydrogen gas, which could reduce cost and environmental impacts.

The decarboxylation process is currently on a laboratory scale. Data was collected in the lab and the yield of renewable hydrocarbons fuel was reported (see chapter 1). The hydrogenation process (HDO) data was gathered from an LCA study done by the Helsinki University of Technology on the Next BTL process at the Neste Oil plant in Kilpilahti [Nikander, 2008].

Goal and Scope

This chapter is not designed to be a complete life cycle assessment, but rather a literature review and look at the potential environmental and economic benefits of a non-hydrogen gas process to produce renewable hydrocarbons. The purpose of this chapter is to better understand the potential impacts of two different paths to renewable diesel production. One is hydrodeoxygenation (HDO) process, which is well known, and the other is a fragment of that reaction, decarboxylation, which has been isolated in this study. Can this one reaction suffice in a commercial scale renewable diesel operation? Will the yields be great enough to make this technology cost competitive, both environmentally and economically, with the better-researched HDO reactor? The stakeholders being addressed through this study are venture capitalists and the fuel production industry. The goal is to compare the energy efficiency and environmental impacts of both HDO and non-hydrogen processes.

System Boundaries

The system boundary for this study is from agriculture to fuel transportation (fig 11). Both processes start with agricultural production of soybean oil and end with renewable diesel (hydrocarbon mix). One process uses only decarboxylation (no hydrogen), and the other uses Hydrogenation/Hydrodeoxygenation (HDO). The functional unit for this LCA is the amount of fuel needed to travel 1 vehicle mile travelled (VMT). This unit is based on previous LCA studies in this field and is an easy to understand unit. For the purpose of this study I gathered data from an LCA study done by the University of Helsinki for all data sets relating to the HDO process [Nikander, 2008]. Lab scale data was used to extrapolate the yields of the decarboxylation process.

A previous LCA study on biodiesel was used for the data for unit processes on agriculture, crushing, and transport [Sheehan, 1998].

Process flow diagram

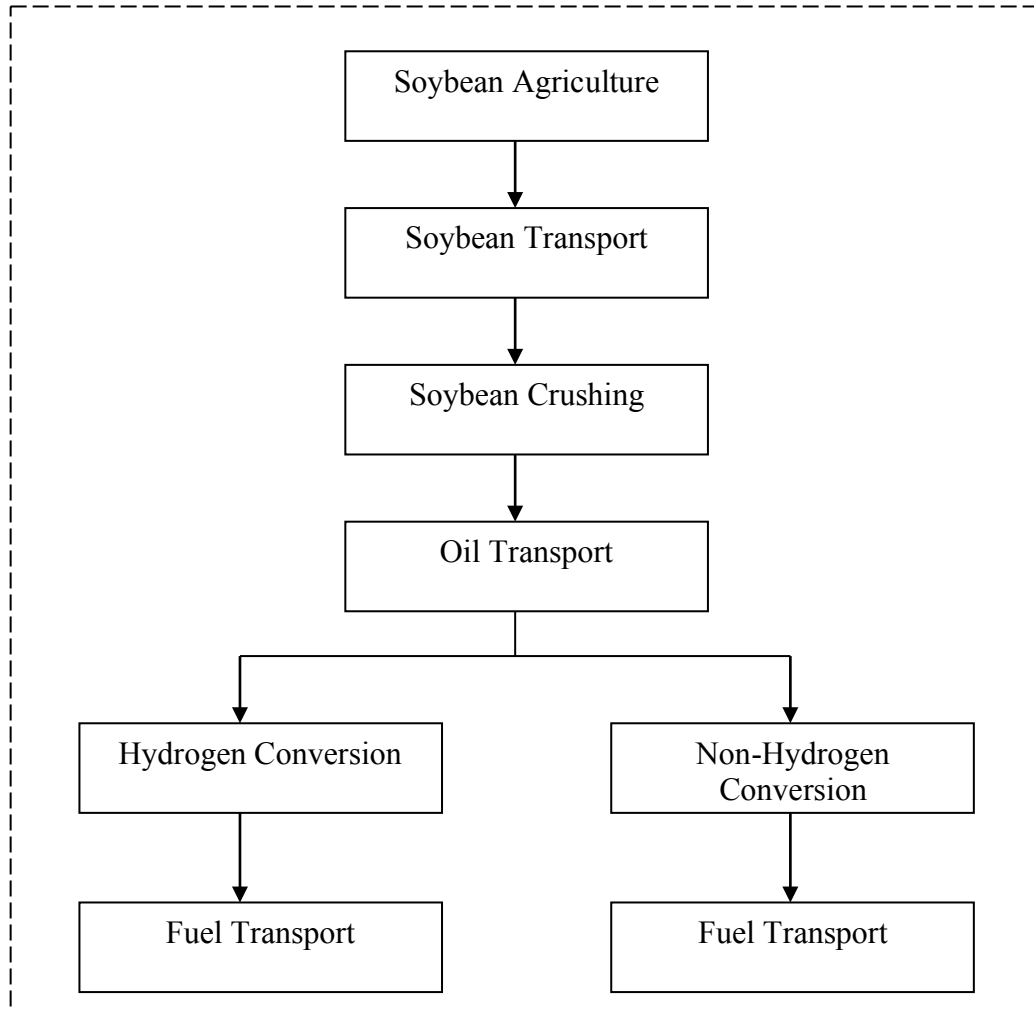


Figure 12 Process Flow Diagram

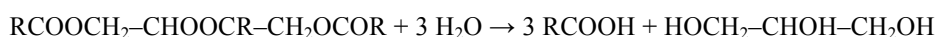
This flow diagram shows the system boundary of the study from agricultural to fuel transportation.

Assumptions and Limitations

Many assumptions were made while compiling this LCA study. These assumptions will be looked at in two major categories: experimental lab data and feedstock selection.

Experimental Lab Data

The single biggest limitation was moving from the laboratory data collected on the non-hydrogen process to a viable comparison with a commercial scale process. I assumed that all inputs for the non-hydrogen process at commercial scale would be the same as reported for the NexBTL process minus the energy and emissions associated with hydrogen gas. Further modeling would be needed for a more accurate representation. Also all experimental data was gathered using fatty acids as model compounds in lieu of using soybean oil. These compounds are similar to soybean oil in composition, but they do not contain glycerin backbones. It was assumed that a hydrolysis step would be added to the industrial reaction scheme to first produce fatty acids from the soybean oil. Fat splitting, or hydrolysis, of triglycerides produces fatty acids and glycerol as seen in reaction below.



My data assumes high yield of fatty acids from soybean oil and therefore might limit the accuracy of the study, but provides a good comparison. Since the conditions for hydrolysis is very similar to decarboxylation (350 C in an aqueous environment with a catalyst) I have considered the GHG emissions associated with hydrolysis to be equivalent to the emissions from the reactor itself [Sinclair et al, 2007]. Another

limitation of this work was that the carbon emissions from the conversion processes were not considered emissions to the air. Since the emissions could be captured during the process, it was assumed that they would be sequestered in some way.

Feedstock

The only feedstock considered was soybean oil. All data on agriculture to refined oil came from data on soybean oil. Other feedstocks would offer different LCA results. All upstream data on unit processes other than the conversion step was gathered from an NREL LCA study on biodiesel [Sheehan, 1998].

Life Cycle Inventory

Allocations

In the LCA study from Helsinki, all beneficial co-products were assessed on their energy and GHG implications by mass balance, or boundary expansion. All impacts were assigned to the primary product. Credits were assigned based on the amount of co-product production. The two major co-products relevant to this analysis are soy meal from the agriculture phase, and fuel gas from the processing phase. The amount of energy and GHG it takes to make an equivalent amount of co-product using the traditional methods was credited to each unit process [Nikander, 2008].

Method of Data Collection

Each unit process presented in the process flow diagram is represented in its own separate table (see appendix). The data for the unit processes for agriculture, transport, and crushing were taken from an LCA study conducted by NREL on biodiesel production [Sheehan, 1998]. Here we assume that these processes will remain the same for

renewable diesel production. All data on input flows relating to the HDO process was acquired from the LCA conducted by University of Helsinki. Output data on CO₂e from the HDO process was reported from the previously mentioned LCA study conducted Helsinki University and based on an 84% yield from pre-treated soybean oil to hydrocarbon fuel [Nikander, 2008]. Other output data for the HDO process was obtained from the NREL LCI database [U.S. LCI Database, 2010]. For the non-hydrogen reaction, process lab scale data on potential yields of hydrocarbon fuel was coupled with the industrial scale process data from the Helsinki LCA study to model production of 1 VMT of fuel quantity. There are many limitations to this approach, but it is the best option available to me since there is no commercial scale data to date on a non-hydrogen process.

All data has been normalized using the functional unit of one vehicle mile traveled (1 VMT). All data streams have been chosen because they are relevant to both processes. All emissions streams were chosen based on a previous LCA study, which examined biodiesel production. Below the data is represented in graphical form (figures 13-15). Data from the five unit processes were taken to mid point indicators using IMPACT 2002.

Decarboxylation Reaction Methods

I used a Parr bench top reactor with a 100 ml reaction vessel to collect data on the non-hydrogen process. During each reaction the vessel was loaded with oleic acid, stearic acid, or linoleic acid and catalyst (20:1 ratio), and the headspace purged with nitrogen [Kinsley, 2001]. At the conclusion of the reaction, all gaseous products were collected in a tedlar bag and analyzed using GC. The liquid products were collected and

analyzed using GD-FID. Based on the findings, the median conversion of a mixture of fatty acids to fuel range hydrocarbons was 45%. Using these numbers and standardizing to 1 VMT of fuel produced the results that are presented in table 3. All data sets on material flows are presented in the appendix.

Conversion Methods

During the course of the study it was appropriate to use different units based on the process being analyzed. All data was eventually converted to 1 vehicle mile traveled. Included below is a chart referencing all relevant conversions made during the study. All numbers were based off of the 25-mpg light truck average in the US [US DOT, 2011].

Table 3 A collection of calculations needed to compute environmental impacts of biofuels.

Variable	value	source
Miles per gallon of petroleum	25 MPG	[10]
1 gallon of Highway Diesel	135.8 MJ	[ORNL, 2008]
1 VMT	Needs 5.432 MJ	[ORNL, 2008]
1 kg soy beans	0.18 kg soy oil	[USDA, 2010]
0.147 kg soy oil (165.7 ml)	1 VMT	calculation
0.139 kg renewable Diesel	1 VMT	[ORNL, 2008]
Denver electricity CO2e emission factor	0.8 kgCO2e/kWh	[Ramaswami, 2008]
Denver electricity emission factor	0.22 kg CO2 e/MJ	calculation
49 MJ	1 kg Natural gas	NREL database
1 kWh	3.6 MJ	[Cengal, 2011]

Environmental Impact Assessment

Emission factors for the unit processes of agriculture, transportation, and crushing were gathered from the NREL LCA study conducted on biodiesel [Sheehan, 1998].

Emission factors for the hydrogen NexBTL process were gathered from two different LCA studies on Neste Oil's plant in Proovo, Finland [Nikander, 2008; Reinhardt, 2006].

All data for the non-hydrogen process was scaled up using the study from Finland and laboratory data on yield and catalysts. Characterization factors came from IMPACT 2002. This study only analyzed mid point categories and did not address damage categories.

Mid Point Impacts analyzed: global warming potential, carcinogenic effects, and aquatic ecotoxicity. The data is reported in the figures below.

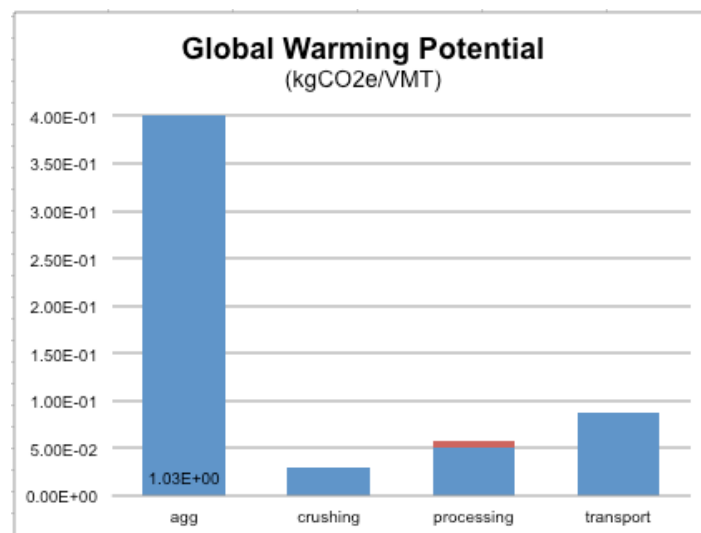


Figure 13 Global Warming Potential Indicator

GWP is reported in carbon dioxide equivalents. All life cycle transportation emissions were combined into one bar. The processing stage has the HDO process in blue on the bottom and the non-hydrogen process in red on top.

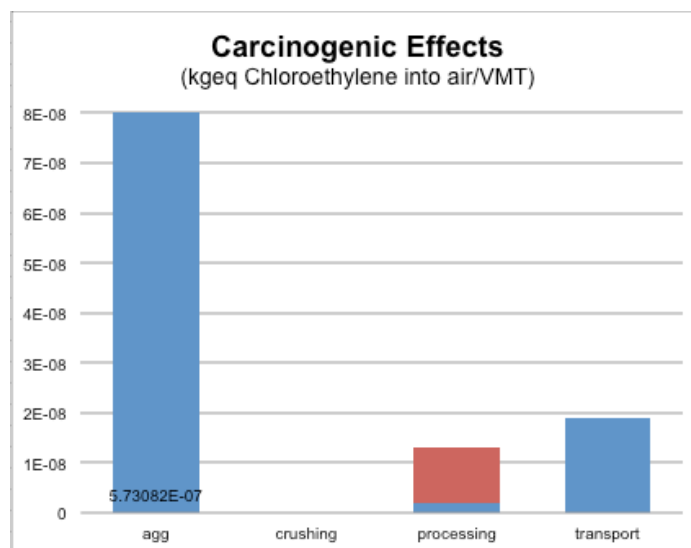


Figure 14 Carcinogenic Effects Indicator

Carcinogenic effects are reported in chloroethylene equivalents. The unit processes are listed separately and all life cycle transportation data is shown in one bar. The processing stage has the HDO process in blue on the bottom and the non-hydrogen process in red on top.

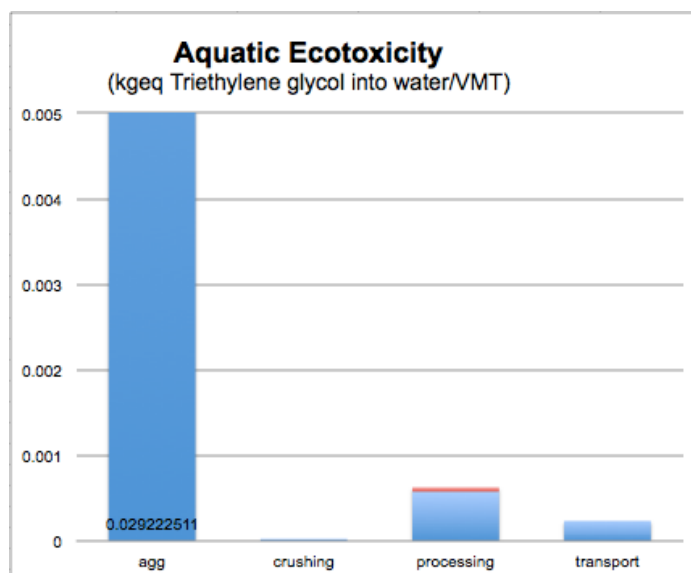


Figure 15 Aquatic Eco Toxicity Indicator

Aquatic eco toxicity is shown as Triethylene glycol equivalents. All unit processes are show separately and life cycle transportation is collected into one bar. The processing stage has the HDO process in blue on the bottom and the non-hydrogen process in red on top.

Table 4 Cradle-to-grave comparison of petroleum diesel, HDO renewable diesel and non-hydrogen renewable diesel

Unit Process	Petroleum diesel		Commercial Renewable Diesel using Hydrogen (HDO)		CU Hydrogen-Free renewable fuel process	
	Energy Inputs MJ/MJ Fuel	Emissions gCO ₂ e/MJ fuel	Energy Inputs MJ/MJ Fu	Emissions gCO ₂ e/MJ fuel	Energy Input MJ/MJ Fuel	Emissions gCO ₂ e/MJ
Agriculture/Mining/Processing						
- Energy	0.03	3.3	0.116	58.69	0.116	58.69
- GHG Emissions						
Transport of Raw Materials						
- Energy	0.01	0.8	0.01	0.3	0.01	0.3
- GHG Emissions						
Processing of Fuel						
- Energy Inputs	0.1	8.6	0.0935	9.33	0.03	2.6
- GHG Emissions						
Transport of Products						
- Energy	0.01	0.7	0.01	0.7	0.01	0.7
- GHG Emissions						
Fuel Use**						
- Energy	-----	73	-----	0	-----	0
- GHG Emissions						
Total	0.15	86.4	0.19	69.86	0.17	62.29

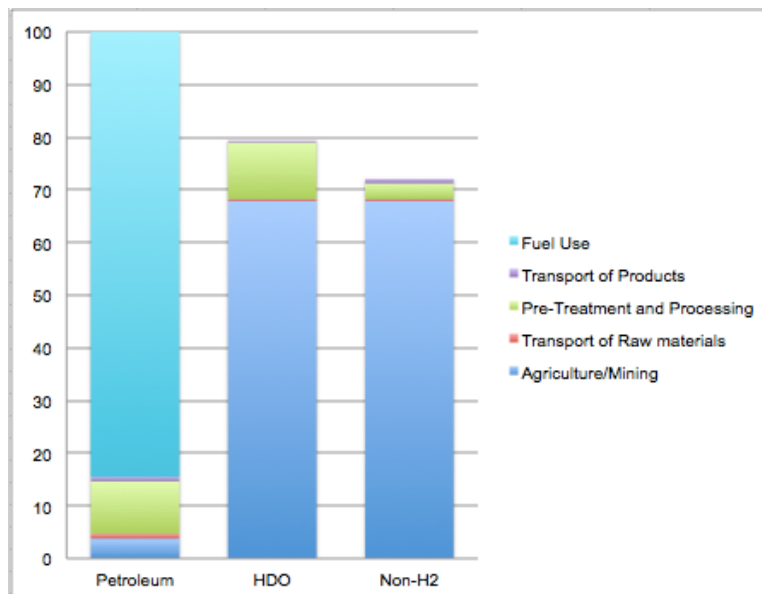


Figure 16 This chart show the life cycle GHG emissions from cradle to grave of three pathways to fuel production normalized to petroleum diesel.

The chart shows that the HDO process has a 20% decrease in life cycle GHG emissions and the un-optimized non-H2 process having a 30% decrease when compared to petroleum diesel.

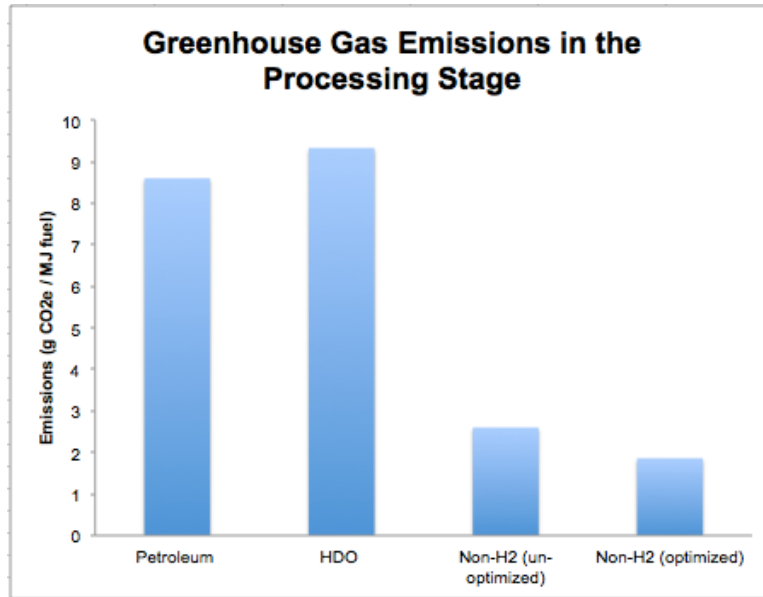


Figure 17 CO_{2e} emissions from only the processing stage of three possible pathways to diesel fuel.

Interpretation

Goal and Scope

The goal of the analysis was to determine which unit process has the greatest impact on the three mid point categories selected: global warming potential (GWP), carcinogenic effects, and aquatic eco toxicity. In addition to determining which unit process had the greatest impact, a direct comparison of two approaches to renewable diesel conversion was analyzed using energy inputs and GHG emissions.

Results and Discussion

This study found that the agricultural phase of the biofuels industry is the largest producer of GHG emissions and therefore has the highest global warming potential. That is comparable with other LCA studies in this field [Sheehan, 1998]. In addition to emitting GHG emissions, agriculture also has the largest impact on ecosystem toxicology and cancer causing substances [figures 14 and 15]. This is mainly due to the energy and fossil fuel intense nature of industrial agriculture as well as runoff to rivers and streams. This study shows that the agriculture industry has more work to be done before being considered a viable alternative to the current petroleum industry. According to the LCI, even with 40% lower yields, the non-hydrogen process had less of an impact on global warming potential and aquatic eco toxicity than did the HDO process. The renewable diesel plant in this study uses natural gas reforming to produce hydrogen, as is the case with most hydrogen production in the world today [Abassi et al, 2011]. Hydrogen production uses large quantities of fossil energy and is responsible for the high GWP and aquatic eco toxicity of the HDO process in addition to contributing to 30% of the financial costs. The carcinogenic mid point indicator showed the HDO process being slightly less harmful than the non-hydrogen process. This is attributed to the increased usage of electricity, both from coal and natural gas, needed in the non-hydrogen process to produce an equivalent yield in biofuel as the HDO process. This resulted in the increased release of cancer causing gasses to the air and eventually into humans. The results from comparing the GHG emissions of the HDO process, the non-hydrogen process, and petroleum diesel are presented in figures 15 and table 4. The data for the petroleum life cycle energy inputs and emission was collected and compiled from an

NREL study comparing petroleum to first generation biodiesel [Sheehan, 1998]. The data for the HDO process and the non-hydrogen process was taken from the Helsinki study [Nikander, 2008]. All of the upstream energy inputs and emissions for the HDO process and the non-hydrogen process are exactly the same. The difference that can be seen between the two renewable diesel processes starts in the processing and pre-treatment stage highlighted in yellow in table 4. Here it can be seen that hydrogen has been removed from the process resulting in a decrease in energy inputs as well as GHG emissions. This decrease is seen even when a 40% drop in biofuel yield from the non-hydrogen process. It can also be seen from figure 16 that the current commercially available HDO renewable diesel processes has higher GHG emissions than even petroleum diesel. This means that the fuel would not qualify as Biomass Based Diesel, which calls for a 50% reduction in life cycle GHG emissions [EPA 2012].

Chapter III

CONCLUSIONS

Significant Findings

The journey towards developing a viable alternative to cheap energy dense fossil fuels is an incremental one. Many research groups and industries are working simultaneously at a multitude of routes for achieving that end. This study has also added to that body of knowledge. Through laboratory experiments, literature review, and environmental assessment, I have verified that a viable alternative drop-in replacement fuel can be produced without the use of hydrogen gas, which in turn could reduce cost and environmental impacts of biofuels.

I have shown that a significant quantity of saturated hydrocarbons can be produced from fatty acids found in soybean oil using the decarboxylation route. This means that the potential for producing biofuels with increasingly lower green house gas emissions and reduced fossil energy inputs is possible. In addition, this study has also directly compared the energy inputs and GHG emissions of petroleum diesel, commercial renewable diesel, and renewable diesel without the use of hydrogen gas. These preliminary findings show that even with an un-optimized reaction, a non-hydrogen process could have half of the emissions of current commercial renewable diesel in the processing stage. As we continue to optimize the reaction and increase yields, energy demands and GHG emission will look even more promising. This shows that it is possible to eliminate the need for large amounts of environmentally detrimental hydrogen gas in commercial scale renewable diesel production.

Next Steps

The results presented in this thesis are exciting and hopeful. But this is just the beginning. The most promising aspect is the capacity building that took place over the course of the research. The Green Engineering and Systems Analysis Lab at CU Denver now has the foundation to build on this research and continue producing state of the art research in advanced biofuels. At the beginning of the research there was a reactor sitting in a corner of a dusty unused lab space. Now the lab is fully equipped to use both batch and semi-batch processes to produce biofuels as well as to analyze and report on the products and results of the reactions. Yield optimization of the reaction is underway, looking at temperature and pressure, as well as catalyst activation/deactivation. At 400 C cracking and isomerization is prevalent, so decreasing the reaction temperature is highly favorable for both product selectivity and energy reduction [Huber, 2007]. More analysis and research needs to be done to further characterize the complete liquid product to better understand the reaction mechanics. In addition, research on a catalytic process to hydrogenate unsaturated feedstock in the reaction vessel is underway. The use of a proton donating solvent has been reported to be effective [Kubic̃kova'etal, 2008]. In addition I plan to employ a food industry process called catalytic transfer hydrogenation as a pre-treatment step. Differing from the classical hydrogenation techniques using molecular hydrogen, hydrogen donors are used as a source of hydrogen in a catalytic transfer reduction to saturate the feedstock. The generalized equation 1 represents this process:



Here “A” represents the acceptor and “D” represents the hydrogen donor [Naglic, 1998]

pg 1; Dumesic, 2011]. This process could greatly decrease the cost and environmental issues with using molecular hydrogen while increasing the yields of fuel range hydrocarbons from the decarboxylation reaction presented in this paper.

Based on these findings we plan to work on catalytic transfer hydrogenation to saturate feedstocks before the decarboxylation reaction. Little work has been done in this realm and it could produce significant increases in yields. In addition we plan to look into wet algae processing for biofuels production. This paper showed that the most significant contributor to life cycle environmental impacts is the agricultural phase. In order to reach the 50% reduction in life cycle GHG emission mandated by the RFS2 fuel standards, much work must be done in the feedstock production realm. Algae are being considered as a possible solution to environmental problems of in-ground agriculture. I have started cultivating strains of algae in the lab and am looking into oil extraction methods as well as wet processing. Now that we have biofuels research capacity at UCD there is limitless directions that we can take the research. Cheers.

REFERENCES

- Abbasi, T., & Abbasi, S. a. (2011). “Renewable” hydrogen: Prospects and challenges. *Renewable and Sustainable Energy Reviews*, 15(6), 3034–3040. doi:10.1016/j.rser.2011.02.026
- Barnes, B., Mathee, A., & Moiloa, K. (2005). Assessing child time-activity patterns in relation to indoor cooking fires in developing countries: a methodological comparison. *International journal of hygiene and environmental health*, 208(3), 219–25. doi:10.1016/j.ijheh.2005.01.022
- Cengel, Yunus A. Boles, Michael A. (2011) Thermodynamics: An Engineering Approach. New York, NY, McGraw-Hill
- Chia, M., & Dumesic, J. a. (2011). Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to γ -valerolactone over metal oxide catalysts. *Chemical communications (Cambridge, England)*, 47(44), 12233–5. doi:10.1039/c1cc14748j
- EPA 1320 SUMMARY : Regulation of Fuels and Fule Additives: 2012 Renewable Fuel Standards (2012).
- Huber, G. W., Iborra, S., & Corma, A. (2006). Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical reviews*, 106(9), 4044–98. doi:10.1021/cr068360d
- Huber, G. W., O’Connor, P., & Corma, A. (2007a). Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Applied Catalysis A: General*, 329, 120–129. doi:10.1016/j.apcata.2007.07.002
- Huber, G. W., O’Connor, P., & Corma, A. (2007b). Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Applied Catalysis A: General*, 329, 120–129. doi:10.1016/j.apcata.2007.07.002
- Kalnes, T. N., Koers, K. P., Marker, T., & Shonnard, D. R. (2009). A Technoeconomic and Environmental Life Cycle Comparison of Green Diesel to Biodiesel and Syndiesel, 28(1), 111–120. doi:10.1002/ep
- Kinsley, G. R. J. (2001). Properly Purge and Inert Storage Vessels. *Chemical Engineering Progress*, 97(2), 57–61.
- Knothe, G. (2010a). Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, 36(3), 364–373. doi:10.1016/j.pecs.2009.11.004

- Knothe, G. (2010b). Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, 36(3), 364–373. doi:10.1016/j.pecs.2009.11.004
- Koloini, T., & Andrej, S. (1998). Kinetics of Catalytic Transfer Hydrogenation. *Journal of American Oil Chemists Society*, 75(5), 629–633.
- Kubičková, I., Snåre, M., Eränen, K., Mäki-Arvela, P., & Murzin, D. Y. (2005). Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. *Catalysis Today*, 106(1-4), 197–200. doi:10.1016/j.cattod.2005.07.188
- Kubickova, I., Snåre, M., Era, K., Murzin, D. Y., & Turku, F.-. (2007). Catalytic Deoxygenation of Fatty Acids and Their Derivatives. *Energy and Fuel*, 21(16), 30–41.
- Mikulec, J., Cvengroš, J., Joríková, L., Banič, M., & Kleinová, A. (2010). Second generation diesel fuel from renewable sources. *Journal of Cleaner Production*, 18(9), 917–926. doi:10.1016/j.jclepro.2010.01.018
- Na, J.-G., Han, J. K., Oh, Y.-K., Park, J.-H., Jung, T. S., Han, S. S., Yoon, H. C., et al. (2012). Decarboxylation of microalgal oil without hydrogen into hydrocarbon for the production of transportation fuel. *Catalysis Today*, 185(1), 313–317. doi:10.1016/j.cattod.2011.08.009
- Na, J.-G., Yi, B. E., Kim, J. N., Yi, K. B., Park, S.-Y., Park, J.-H., Kim, J.-N., et al. (2010). Hydrocarbon production from decarboxylation of fatty acid without hydrogen. *Catalysis Today*, 156(1-2), 44–48. doi:10.1016/j.cattod.2009.11.008
- Nikander, S. (2008). *GREENHOUSE GAS AND ENERGY INTENSITY OF PRODUCT CHAIN : CASE TRANSPORT BIOFUEL*. Helsinki University of Technology.
- Oak Ridge National Laboratory (2008), Conversion Factors for Bioenergy, retrieved from www.ces.ncsu.edu/forestry/biomass.html
- Paula, Matthew de (2011). Veggie Oil Smells Better Than Diesel, But It's No Slam Dunk. Forbes,. Retrieved from <http://www.forbes.com/sites/matthewdepaula/2011/05/27/veggie-oil-might-smell-better-than-diesel-but-its-no-slam-dunk/>
- Pearlson, M. N. (2011). *A Techno-Economic and Environmental Assessment of Hydroprocessed Renewable Distillate Fuels* by. MIT.
- Ramaswami, A., Hillman, T., Janson, B., Reiner, M., & Thomas, G. (2008). Policy Analysis A Demand-Centered , Hybrid Life-Cycle Methodology for City-Scale Greenhouse Gas Inventories. *American Chemical Society*, 42(17), 6455–6461.

- Reinhardt, G. (2006). *Final Report An Assessment of Energy and Greenhouse Gases of NExBTL* (pp. 1–30). Porvoo, Finland.
- REN21. (2011). *Renewables 2011 Global Status Report* (pp. 1–116). Retrieved from www.ren21.net
- Roh, H.-S., Eum, I.-H., Jeong, D.-W., Yi, B. E., Na, J.-G., & Ko, C. H. (2011). The effect of calcination temperature on the performance of Ni/MgO–Al₂O₃ catalysts for decarboxylation of oleic acid. *Catalysis Today*, 164(1), 457–460. doi:10.1016/j.cattod.2010.10.048
- Rozmyszowicz, B., Lestari, S., Simakova, O., Er, K., Salmi, T., & Murzin, D. Y. (2011). Catalytic Deoxygenation of Tall Oil Fatty Acid over Palladium Supported on Mesoporous Carbon. *Energy and Fuels*, (25), 2815–2825.
- Schlagemann, P., Göttlicher, G., Dillschneider, R., Rosello-Sastre, R., & Posten, C. (2012). Composition of Algal Oil and Its Potential as Biofuel. *Journal of Combustion*, 2012, 1–14. doi:10.1155/2012/285185
- Senate Low Aromatic Fuel Act 2013 (2013). Retrieved from www.comlaw.gov.au/
- Şenol, O., Ryymin, E.-M., Viljava, T.-R., & Krause, a. O. I. (2007). Effect of hydrogen sulphide on the hydrodeoxygenation of aromatic and aliphatic oxygenates on sulphided catalysts. *Journal of Molecular Catalysis A: Chemical*, 277(1-2), 107–112. doi:10.1016/j.molcata.2007.07.033
- Serrano-Ruiz, J. C., Pineda, A., Balu, A. M., Luque, R., Campelo, J. M., Romero, A. A., & Ramos-Fernández, J. M. (2012). Catalytic transformations of biomass-derived acids into advanced biofuels. *Catalysis Today*, 195(1), 162–168. doi:10.1016/j.cattod.2012.01.009
- Sheehan, J. et al. (1998). *Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus* (pp. 1–314).
- Šimáček, P., Kubička, D., Šebor, G., & Pospíšil, M. (2009). Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel. *Fuel*, 88(3), 456–460. doi:10.1016/j.fuel.2008.10.022
- Sinclair, C., & Manager, E. (2007). *Cremation of Human Remains : A Comparison of Alkaline Hydrolysis versus Combustion* (pp. 1–6). Retrieved from www.resomation.com
- Snåre, M., Kubičková, I., Mäki-Arvela, P., Chichova, D., Eränen, K., & Murzin, D. Y. (2008). Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons. *Fuel*, 87(6), 933–945. doi:10.1016/j.fuel.2007.06.006

- Snåre, M., Kubičková, I., Mäki-Arvela, P., Eränen, K., Wärnå, J., & Murzin, D. Y. (2007). Production of diesel fuel from renewable feeds: Kinetics of ethyl stearate decarboxylation. *Chemical Engineering Journal*, 134(1-3), 29–34. doi:10.1016/j.cej.2007.03.064
- Solecki, M., & Epstein, B. (2011). *Advanced Biofuel Market Report 2011 Meeting the California LCFS Authors Table of Contents* (pp. 1–22).
- Tat, M. E., Wang, P. S., Gerpen, J. H., & Clemente, T. E. (2007). Exhaust Emissions from an Engine Fueled with Biodiesel from High-Oleic Soybeans. *Journal of the American Oil Chemists' Society*, 84(9), 865–869. doi:10.1007/s11746-007-1109-6
- U.S. Department of Agriculture (2010), Soybeans and Oil Crops: Background. Retrieved from: <http://www.ers.usda.gov/Briefing/SoybeansOilcrops/background.htm>
- U.S. Department of Transportation, Federal Highway Administration, (2011) *Highway Statistics* (Washington, DC: Annual Issues), table VM-1, available at <http://www.fhwa.dot.gov/policyinformation/statistics.cfm>
- "U.S. Life Cycle Inventory Database." (2012). National Renewable Energy Laboratory, 2012. Accessed November 19, 2012: <https://www.lcacommons.gov/nrel/search>
- Veriansyah, B., Han, J. Y., Kim, S. K., Hong, S.-A., Kim, Y. J., Lim, J. S., Shu, Y.-W., et al. (2012). Production of renewable diesel by hydroprocessing of soybean oil: Effect of catalysts. *Fuel*, 94, 578–585. doi:10.1016/j.fuel.2011.10.057
- Wang, W.-C., Roberts, W. L., & Stikeleather, L. F. (2012). Hydrocarbon Fuels From Gas Phase Decarboxylation of Hydrolyzed Free Fatty Acid. *Journal of Energy Resources Technology*, 134(3), 032203. doi:10.1115/1.4006867
- Wang, W.-C., Thapaliya, N., Campos, A., Stikeleather, L. F., & Roberts, W. L. (2012). Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation. *Fuel*, 95, 622–629. doi:10.1016/j.fuel.2011.12.041

APPENDIX

Soybean Agriculture Unit Process Data

This includes fuels, fertilizers, and inputs used on the farm and their associated emissions, as well as the upstream emissions associated with those inputs used to grow soybeans. These upstream environmental flows are combined with the flows associated with the actual soybean growing and harvesting to calculate the total emissions associated with soybean agriculture [Sheehan, 1998]. All data has been normalized to 1 VMT.

Table 5 Soybean agriculture raw materials data

Raw Materials for Soybean Agriculture	Units	kg of raw material/ 1 VMT
Coal (in ground)	kg	0.0474376
Oil (in ground)	kg	0.2439248
Natural Gas (in ground)	kg	0.0928704
Uranium (U, ore)	kg	0.000002604
Phosphate Rock (in ground)	kg	0.335776
Potash (K ₂ O, in ground)	kg	0.1578192
Perlite (SiO ₂ , ore)	kg	0.000047544
Limestone (CaCO ₂ , in ground)	kg	0.0061376
Sodium Chloride (NaCl)	kg	0
Water Use	kg	3081.96
Elec from Coal	kg	2.44048
Elec from Natural gas	kg	2.44048

Table 6 Soybean agriculture emissions data

Emissions from Soybean Agriculture	Units	Total emissions / 1 VMT
AIR		
Carbon Dioxide (CO ₂ , fossil)	kg	1.024072
Carbon Dioxide (CO ₂ , biomass)	kg	0
Methane (CH ₄)	kg	0.001012592
Nitrous Oxide (N ₂ O)	kg	0.00004676
Carbon Monoxide (CO)	kg	0.004890312
Hydrocarbons	kg	0.006069504
Benzene	kg	4.6928E-08
Formaldehyde	kg	6.328E-07
Particulates, unspecified	kg	0.001043084
Sulfur oxides	kg	0.003357558
Nitrogen oxides	kg	0.007168
Hydrogen chloride	kg	0.00000952
Hydrogen fluoride	kg	4.3848E-07
Ammonia (air)	kg	0.0026208

WATER		
Agrochemicals	kg	0.00037352
BOD5	kg	0.000189896
COD	kg	0.00134624
Metals	kg	0.000005824
Ammonia	kg	0.000022512
Nitrates	kg	9.576E-08

Soybean Transport Unit Process Data

The transport of soybeans from the field to the crusher is based on current practices in the soybean farming and soybean crushing sectors. The actual data used in this study were based on a combination of conversations with industry representatives and modeled data. They ignored transporting soybeans for the export market, which represents the longest transportation distances in the industry [Sheehan, 1998].

Table 7 Soybean transport raw materials data

Raw Materials for Soybean Transport	Units	Kg of material / 1 VMT
Coal (in ground)	kg	0.00059472
Oil (in ground)	kg	0.01903664
Natural Gas (in ground)	kg	0.00163464
Uranium (U, ore)	kg	1.316E-08
Phosphate Rock (in ground)	kg	0
Potash (K ₂ O, in ground)	kg	0
Perlite (SiO ₂ , ore)	kg	0.000004088
Limestone (CaCO ₂ , in ground)	kg	0.00011312
Sodium Chloride (NaCl)	kg	0
Water Use	kg	0.00264936
Elec from Coal	kg	0.126017889
Elec from Natural gas	kg	0.126017886

Table 8 Soybean transport emissions data

Emissions from Soybean Transport	Units	Total emissions / 1 VMT
AIR		

Carbon Dioxide (CO₂, fossil)	kg	0.0634228
Carbon Dioxide (CO₂, biomass)	kg	0
Methane (CH₄)	kg	2.27276E-05
Nitrous Oxide (N₂O)	kg	6.30168E-06
Carbon Monoxide (CO)	kg	0.00021512
Hydrocarbons	kg	0.0000714
Benzene	kg	4.2728E-09
Formaldehyde	kg	5.712E-08
Particulates, unspecified	kg	8.54661E-05
Sulfur oxides	kg	0.000093408
Nitrogen oxides	kg	0.00059673
Hydrogen chloride	kg	3.192E-07
Hydrogen fluoride	kg	3.9928E-08
Ammonia (air)	kg	8.12E-11
WATER		
Agrochemicals	kg	0
BOD5	kg	0.000012768
COD	kg	0.000108024
Metals	kg	5.2808E-07
Ammonia	kg	1.86704E-06
Nitrates	kg	5.0568E-10

Soybean Crushing Unit Process Data

The crushing process in this study is assumed to be representative of typical soybean crushing operations in the United States. The major distinguishing feature among the types of processes used in the U.S. crushing plants is in the oil extraction method. Our model facility uses solvent extraction to recover the oil. The other major method for extraction is mechanical crushing. Only 1% to 2% of the soybeans processed in the United States are recovered via mechanical extraction methods [Sheehan, 1998]

Table 9 Soybean crushing raw materials data

Raw Materials for Soybean Crushing	Units	Raw materials / 1 VMT
Coal (in ground)	kg	0.019754224
Oil (in ground)	kg	0.003182424
Natural Gas (in ground)	kg	0.053525584
Uranium (U, ore)	kg	4.7348E-07
Phosphate Rock (in ground)	kg	0
Potash (K₂O, in ground)	kg	0
Perlite (SiO₂, ore)	kg	0
Limestone (CaCO₂, in ground)	kg	0.00376656

Sodium Chloride (NaCl)	kg	0
Water Use	kg	0.004359208
Elec from Coal	kg	0.508763304
Elec from Natural gas	kg	0.508763304

Table 10 Soybean crushing emissions data

Emissions from Soybean Crushing	Units	Total emissions from Agg/ 1 VMT
AIR		
Carbon Dioxide (CO ₂ , fossil)	kg	0.21234768
Carbon Dioxide (CO ₂ , biomass)	kg	0
Methane (CH ₄)	kg	0.000395656
Nitrous Oxide (N ₂ O)	kg	1.92284E-06
Carbon Monoxide (CO)	kg	6.43876E-05
Hydrocarbons	kg	0.001979569
Benzene	kg	0
Formaldehyde	kg	3.18E-15
Particulates, unspecified	kg	0.000281171
Sulfur oxides	kg	0.001516627
Nitrogen oxides	kg	0.000398267
Hydrogen chloride	kg	1.06201E-05
Hydrogen fluoride	kg	1.32712E-06
Ammonia (air)	kg	4.8972E-08
WATER		
Agrochemicals	kg	0
BOD ₅	kg	2.6818E-07
COD	kg	2.19314E-06
Metals	kg	6.2858E-08
Ammonia	kg	3.53404E-07
Nitrates	kg	1.6854E-08

Soybean Oil Transport Unit Process Data

The NREL LCA practitioners studied average transport distances for soybean oil in depth. This data includes average fuel emissions from wells to pump and pump to wheels [Sheehan, 1998].

Table 11 Soybean transport data raw materials

Raw Materials for Soybean Oil Transport	Units	Kg of raw material / 1 VMT
---	-------	----------------------------

Coal (in ground)	kg	0.00021702
Oil (in ground)	kg	0.006945164
Natural Gas (in ground)	kg	0.000596416
Uranium (U, ore)	kg	5.1072E-09
Phosphate Rock (in ground)	kg	0
Potash (K ₂ O, in ground)	kg	0
Perlite (SiO ₂ , ore)	kg	1.57472E-06
Limestone (CaCO ₂ , in ground)	kg	4.11768E-05
Sodium Chloride (NaCl)	kg	0
Water Use	kg	0.000966573
Elec from Coal	kg	0.0459648
Elec from Natural gas	kg	0.0459648

Table 12 Soybean transport emissions data

Emissions from Soybean Oil Transport	Units	Total emissions from Oil Transport / 1 VMT
AIR		
Carbon Dioxide (CO ₂ , fossil)	kg	0.023296044
Carbon Dioxide (CO ₂ , biomass)	kg	0
Methane (CH ₄)	kg	8.37718E-06
Nitrous Oxide (N ₂ O)	kg	2.4839E-07
Carbon Monoxide (CO)	kg	7.77499E-05
Hydrocarbons	kg	2.80794E-05
Benzene	kg	1.5476E-09
Formaldehyde	kg	2.0776E-08
Particulates, unspecified	kg	1.42888E-05
Sulfur oxides	kg	3.39094E-05
Nitrogen oxides	kg	0.00038425
Ammonia (air)	kg	2.9574E-11
WATER		
Agrochemicals	kg	0
BOD ₅	kg	4.64074E-06
COD	kg	3.92678E-05
Metals	kg	1.9193E-07
Ammonia	kg	1.8338E-10
Nitrates	kg	1.5052E-08

Soybean Oil Conversion to Renewable Diesel using Hydrogen Process

This data set includes the energy use from the HDO reaction at the NESTE Oil plant in Finland plus all inputs from production of hydrogen gas [Nikander, 2008].

Table 13 HDO raw materials data assuming an 84% yield

Raw Materials for HDO conversion	Units	Kg of raw material / 1 VMT
Treated Soybean Oil	kg	0.14699
Natural Gas (for hydrogen)	kg	0.00588
Fuel Gas (for hydrogen)	kg	0.00196
Process Water	kg	0.02861
Cooling water Use	kg	0.0004887
Steam	MJ	0.003801
Elec from Coal	kWh	0.00332
Elec from Natural gas	kWh	0.00332

Table 14 HDO emissions data assuming an 84% yield

Emissions	Units	Total emissions from Agg/ 1 VMT
AIR		
CO2e (from electricity)	kg	0.0011
CO2e (from Steam)	kg	0.00396
CO2e (from hydrogen)	kg	0.04561
Methane (CH4)	kg	2.37478E-05
Nitrous Oxide (N2O)	kg	0
Carbon Monoxide (CO)	kg	3.31169E-06
Hydrocarbons	kg	0
Benzene	kg	1.87249E-09
Formaldehyde	kg	2.33507E-09
Particulates, unspecified	kg	2.95796E-07
Sulfur oxides	kg	0.002156816
Nitrogen oxides	kg	3.11198E-06
Ammonia (air)	kg	0
		0
WATER		0
Agrochemicals	kg	1.7376E-08
BOD5	kg	0
COD	kg	2.37478E-05
Metals	kg	0
Ammonia	kg	3.31169E-06
Nitrates	kg	0

Soybean Oil Conversion to Renewable Diesel using Non-Hydrogen Process

This data set looks at all inputs and relevant outputs from the lab scale yield data overlaid on the process data from the Neste Oil plant [Nikander, 2008].

Table 15 Non-hydrogen raw materials data assuming a 45% yield

Raw Materials for Non-H2 conversion	Units	Kg of raw material / 1 VMT
Treated Soybean Oil	kg	0.1940268
Palladium on Carbon	kg	0.0096888
Process Water	kg	0.0377652
Cooling water Use	kg	0.000645084
Steam	MJ	0.00501732
Elec from Coal	kWh	0.0043824
Elec from Natural gas	kWh	0.0043824

Table 16 Non-hydrogen emissions data assuming a 45% yield

Emissions	Units	Total emissions from Agg/ 1 VMT
AIR		
CO2e (from electricity)	kg	0.00151
CO2e (from Steam)	kg	0.00554
CO2e (from Palladium)	kg	0.0000015
Methane (CH4)	kg	2.99515E-05
Nitrous Oxide (N2O)	kg	0
Carbon Monoxide (CO)	kg	4.20173E-06
Hydrocarbons	kg	0
Benzene	kg	2.35595E-09
Formaldehyde	kg	2.93798E-09
Particulates, unspecified	kg	2.60605E-05
Sulfur oxides	kg	0.002713707
Nitrogen oxides	kg	4.35272E-06

Ammonia (air)	kg	0
WATER		
Agrochemicals	kg	0
BOD5	kg	0
COD	kg	0
Metals	kg	0
Ammonia	kg	2.18624E-08
Nitrates	kg	7.10528E-12